博 士 論 文 内 容 の 要 旨

専攻名 物質工学

講座名 分子工学

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１ 論文題目（英文の場合は，和訳を付記すること）

Flaky graphene facilitating electrochemical reactions of polyaniline

（ポリアニリンの電気化学反応を促進する片状グラフェン）

２ 要 旨（和文 2,000 字程度又は英文 800 語程度にまとめること。）

Polyanline (PANI) is an electrically conducting polymer. The conductivity can readily be controlled with electrochemically redox reactions. When graphene (GN) flakes, a carbon material, are incorporated into PANI, the formed PANI-GN composite has enhanced the electrical conductivity, catalytic activity, capacitances, and electrochemical cycling stability. The synergetic effects have been used to expound the enhancement without being specified from a quantitative viewpoint.

The aim of the dissertation is to specify functionalities of GN at the electrochemical reaction of PANI in the composite not only by the voltammetry of PANI-GN particle suspensions but also by measurements of the growth rate of the conducting zone of PANI in PANI-GN film. GN was obtained by reducing the dispersed graphene oxide (GO) solution by chemical reductions. GO was generated by oxidizing graphite powder. The PANI-GN suspension, which was prepared by reducing composite particles of PANI coating GO, exhibited both the reduction and the oxidation waves, whereas the PANI-GO suspension showed only the voltammetric reduction wave. The reduction or oxidation peak currents were controlled by diffusion of the composite particles. The PANI-GN film which was papered by drying the PANI-GN suspension formed a self-standing, elastic, conductive film. The voltammetric current of PANI-GN film cast on the electrode was 4.5 times larger than that of the PANI-GO film with the common weight of PANI. This fact can be explained in terms of the

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electrochemically exhaustive oxidation of PANI through the electric conduction of GN. The PANI-GN film also exhibited faster electrochemical conversion than the PANI film. A reason of the enhancement of the conversion rate is searched by examining the growth rates of the conducting zone which appeared at the boundary between the oxidized and the reduced PANI in the film when the reduced composite was oxidized electrochemically from one end of the film. Higher anodic potentials and higher ratio of GN fractions enhanced the growth rates. There are several possible reasons for the increase in the rates: electro-catalytic properties for the oxidation, enhancement of the conductivity by GN, the electric percolation, and enhancement of specific surface area of GN. The growth rate was modeled with the oxidation at the Tafel-typed rate, which was restrained by the IR-drop between the conducting front and the electrode. The growth length was expressed by a time-dependent non-linear differential equation. The numerical solution allowed us to analyze the experimental data of the time variation of the growth length. GN functions as an increase in the rough surface area of the oxidation rather than electric percolation, enhancement of conductivity and catalytic effects.

Chapter 1 describes electric and electrochemical properties of PANI and PANI-GN composite. Chapter 2 gives the detail of the experimental process. The next chapters are the redox reaction of PANI-GN particles in suspension (Chapter 3) and the propagation of the conducting zone of PANI in PANI-GN film (Chapter 4). The conclusion part is in Chapter 5.

Chapter 3 reports the PANI-GN and PANI-GO flaky particles dispersed well in 1 M acid aqueous solution. The weight fraction of PANI has a saturated value for the loaded fraction is larger than 0.4. The SEM give the morphology of PANI-GN and PANI-GO, indicating PANI is uniformly coated on GO or GN. The UV-vis spectra give the information of the oxidation state of the synthesized PANI which demonstrates that the PANI-GO and PANI-GN hybrids are formed. The redox charge of PANI-GN film cast on the electrode is measured. The difference in voltammetric waves of PANI-GO and PANI-GN suspensions can be explained as the electric conductive GN making the reduced PANI to be oxidized electrochemically. This is the role of GN flakes in the redox reaction of PANI in the PANI-coated GN particles in suspension.

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Chapter 4 deals with facilitation of the electrochemical conversion rate of conducting zone of PANI. The PANI-GN film showed a clear moving boundary between the dark blue in the reduced (insulating) zone and the brown in the oxidized (conducting) zone. The growth rate of conducting zone of PANI in PANI-GN film is faster than that of the PANI film. The theory of the growth of conducting zone of PANI is proposed. Analysis of the experimental data of the time variation of the growth length clarifies the mechanisms of the enhancement.